

WHAT IS CLAIMED IS:

1. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a compound having the formula LiMPO_4 , where M is at least one first-row transition-metal cation.
- 5 2. The cathode material of claim 1, where M is further defined as being selected from the group consisting of Mn, Fe, Co, and Ni
3. The cathode material of claim 1, where M is further defined as being a combination of cations, at least one of which is selected from the group consisting of Mn, Fe, Co and Ni.
- 10 4. The cathode material of claim 3, where M is $\text{Fe}_{1-x}\text{Mn}_x$ or $\text{Fe}_{1-x}\text{Ti}_x$ and $0 < x < 1$.
5. The cathode material of claim 2, wherein the cathode material has the formula LiFePO_4 .
- 15 6. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a rhombohedral NASICON material having the formula $\text{Y}_x\text{M}_2(\text{PO}_4)_3$, where M is at least one first-row transition-metal cation and $0 \leq x \leq 5$ and Y is Li or Na.
- 20 7. The cathode material of claim 5, where M is selected from the group consisting of Fe, V, Mn, and Ti.
8. The cathode material of claim 7, wherein the cathode material has the formula $\text{Li}_{3+x}\text{Fe}_2(\text{PO}_4)_3$, where $0 \leq x \leq 2$.
- 25 9. The cathode material of claim 7, wherein the cathode material has the formula $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$.
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10. The cathode material of claim 7, having the formula $\text{Li}_{1+x}\text{Ti}_2(\text{PO}_4)_3$.

11. The cathode material of claim 7, having the formula $\text{Li}_2\text{FeTi}(\text{PO}_4)_3$.

5 12. The cathode material of claim 7, having the formula $\text{Li}_x\text{TiNb}(\text{PO}_4)_3$, where $0 \leq x \leq 2$.

13. The cathode material of claim 7, having the formula $\text{Li}_{1+x}\text{FeNb}(\text{PO}_4)_3$, where $0 \leq x \leq 2$.

14. The cathode material of claim 7, prepared by the process comprising the steps:

- 10 (a) preparing $\text{Na}_2\text{Fe}_2(\text{PO}_4)_3$; and
(b) contacting said $\text{Na}_2\text{Fe}_2(\text{PO}_4)_3$ with a molten lithium salt, such that an ionic exchange reaction occurs.

15 15. The cathode material of claim 7, prepared by a direct solid state reaction.

16. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a rhombohedral NASICON material having the formula $\text{Y}_x\text{M}_2(\text{PO}_4)_y(\text{XO}_4)_{3-y}$, where $0 < y \leq 3$, M is a transition-metal atom, $0 \leq x \leq 5$, Y is Li or Na, and X = Si, As, or S.

20 17. The cathode material of claim 16, wherein the cathode material has the formula $\text{Li}_{1+x}\text{Fe}_2(\text{SO}_4)_2(\text{PO}_4)$, where $0 \leq x \leq 2$.

18. The cathode material of claim 17, prepared by the process comprising the steps:

- 25 (a) preparing an aqueous solution comprising FeCl_3 , $(\text{NH}_4)_2\text{SO}_4$, and LiH_2PO_4 ;
(b) evaporating the solution to obtain dry material; and
(c) heating the dry material to about 500°C .

19. A cathode material for a rechargeable electrochemical cell also comprising an anode and an electrolyte, the cathode comprising a rhombohedral NASICON material having the formula $A_{3-x}V_2(PO_4)_3$, where A may be Li, Na or a combination thereof and $0 \leq x \leq 2$.

5 20. The cathode material of claim 19, wherein the cathode material has the formula $Li_xNaV_2(PO_4)_3$, where $0 \leq x \leq 2$.

21. The cathode material of claim 19, prepared by the process comprising the steps:

- 10 (a) preparing $Na_3V_2(PO_4)_3$; and
(b) contacting said $Na_3V_2(PO_4)_3$ with a molten lithium salt, such that an ionic exchange reaction occurs.

22. The cathode material of claim 19, prepared by a direct solid-state reaction.

15 23. A cathode material for a rechargeable electrochemical cell, said cell also comprising an anode and an electrolyte, the cathode material comprising a compound having the formula:



where

20 M may be Fe^{2+} or Mn^{2+} or mixtures thereof;

D is a metal in the +2 oxidation state selected from the group consisting of: Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Cu^{2+} , and Ti^{2+} ;

T is a metal in the +3 oxidation state selected from the group consisting of: Al^{3+} , Ti^{3+} , Cr^{3+} , Fe^{3+} , Mn^{3+} , Ga^{3+} , Zn^{2+} , and V^{3+} ;

25 Q is a metal in the +4 oxidation state selected from the group consisting of: Ti^{4+} , Ge^{4+} , Sn^{4+} , and V^{4+} ;

R is a metal in the +5 oxidation state selected from the group consisting of: V^{5+} , Nb^{5+} , and Ta^{5+} ;

$0 \leq x \leq 1$;

0 ≤ y, d, t, q, r, p, s, v ≤ 1 where at least one of y, d, t, q, r, p, s, and v differ from 0 and

$$y + d + t + q + r \leq 1;$$

$$p + s + v \leq 1; \text{ and}$$

$$3 + s - p = x - y + t + 2q + 3r;$$

where x is the degree of intercalation during operation of the electrode material, y represents the fraction of lithium ions on the initial Fe²⁺ sites; d represents the fraction of divalent ions (noted as D) on the initial Fe²⁺ sites; t represents the fraction of trivalent ions (noted as T) on the initial Fe²⁺ sites; q represents the fraction of tetravalent ions (noted as Q) on the initial Fe²⁺ sites; r represents the fraction of pentavalent ions (noted as R) on the initial Fe²⁺ sites; p represents the fraction of hexavalent sulfur (as discrete SO₄²⁻ tetrahedra) on the initial P⁵⁺ sites; s represents the fraction of tetravalent silicon (as discrete SiO₄²⁻ tetrahedra) on the initial P⁵⁺ sites; and v represents the fraction of pentavalent vanadium ions on the initial P⁵⁺ sites, and M, D, T, Q and R reside in octahedral sites.

24. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising an ordered olivine compound having the formula LiMPO₄, where M is at least one first-row transition-metal cation.

25. The battery of claim 23, where M is further defined as being selected from the group consisting of Mn, Fe, Co, and Ni.

26. The battery of claim 23, where M is further defined as being a combination of cations, at least one of said cations being selected from the group consisting of Mn, Fe, Co, and Ni.

27. The battery of claim 23, wherein M is Fe_{1-x}Mn_x or Fe_{1-x}Ti_x, where 0 ≤ x ≤ 1.

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28. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising a modified olivine compound as set forth in claim 23.

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29. The battery of claim 28, wherein the anode comprises a compound selected from the group consisting of a metallic lithium, a lithium alloy, a lithium-carbon intercalation compound, a lithium-transition metal mixed nitride of antiferite and a lithium-titanium spinel having the formula $\text{Li}_{1+x} \text{Ti}_2 \text{O}_4$ where $0 \leq x \leq 1/3$ and $0 \leq z \leq 1 - 2x$.

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30. The battery of claim 29, wherein said cathode further comprises a conductive additive.

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31. The battery of claim 30, wherein said conductive additive is carbon.

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32. The battery of claim 31, wherein said cathode further comprises an intercalation material with fast diffusion kinetics.

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33. The battery of claim 32, wherein said intercalation material is selected from the group consisting of a lamellar dichalcogenide, a vanadium oxide having the formula VO_x where $2.1 \leq x \leq 2.5$, and a NASICON-related material.

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34. The battery of claim 33, wherein said NASICON-related material is selected from the group consisting of $\text{Li}_3\text{Fe}_2(\text{PO}_4)_3$ and $\text{Li}_3\text{Fe}_2\text{Ti}(\text{PO}_4)_3$.

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35. The battery of claim 34, wherein said cathode further comprises a polymeric binder.

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36. The battery of claim 35, wherein said polymeric binder is selected from the group consisting of a homopolymer of tetrafluoroethylene, a copolymer of tetrafluoroethylene, an ethylene-propylene-diene terpolymer, a polyether, a polyester, a methylmethacrylate-based polymer, an acrylonitrile-based polymer, and a vinylidene fluoride-based polymer.

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37. The battery of claim 36, wherein said polymeric binder is a polyether.

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38. The battery of claim ~~37~~, wherein said polyether further comprises a salt comprising Li⁺ cations.

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5 ~~39~~. The battery of claim ~~38~~, wherein said polyether is crosslinked.

A 40. The battery of claim 35, wherein said ~~polymeric binder~~ has an ionic conductivity of between about 10^{-7} and about 10^{-2} (S cm^{-1}) ~~at room temperature~~

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10 ~~41~~. The battery of claim ~~38~~, wherein said polymeric binder is swollen by an aprotic solvent.

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15 ~~42~~. The battery of claim ~~41~~, wherein said aprotic solvent is selected from the group consisting of: ethylene carbonate, propylene carbonate, dimethylcarbonate, diethylcarbonate, methyl-ethylcarbonate, γ -butyrolactone, a tetraalkylsulfamide, a dialkylether of an ethylene glycol having a molecular weight ≤ 2000 .

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~~43~~. The battery of claim ~~42~~, wherein said aprotic solvent is a dialkylether of an ethylene glycol having a molecular weight ≤ 2000 .

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20 ~~44~~. The battery of claim ~~43~~, wherein said dialkylether comprises a mono-ethylene glycol.

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~~45~~. The battery of claim ~~43~~, wherein said dialkylether comprises a di-ethylene glycol.

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25 ~~46~~. The battery of claim ~~43~~, wherein said dialkylether comprises a tri-ethylene glycol.

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~~47~~. The battery of claim ~~43~~, wherein said dialkylether comprises a tetra-ethylene glycol.

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30 ~~48~~. The battery of claim ~~43~~, wherein said dialkylether comprises an oligo-ethylene glycol higher than a tetra-ethylene glycol.

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49. The battery of claim 42, wherein said dialkylether comprises a mixture of mono-, di-, tri-, tetra-, and higher oligo-ethylene glycols.

5 50. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising a rhombohedral NASICON material having the formula $Y_xM_2(PO_4)_3$, where M is at least one first-row transition-metal cation and $0 \leq x \leq 5$ and Y is Li or Na, other than $Li_{2+x}FeTi(PO_4)_3$.

10 51. The battery of claim 27, where M is selected from the group consisting of Fe, V, Mn, and Ti.

52. The battery of claim 28, wherein the cathode material has the formula $Li_{3+x}Fe_2(PO_4)_3$, where $0 \leq x \leq 2$.

15 53. The battery of claim 29, wherein the cathode material has the formula $Li_3Fe_2(PO_4)_3$.

54. The battery of claim 28, wherein the cathode material has the formula $Li_2FeTi(PO_4)_3$.

20 55. The battery of claim 28, wherein the cathode material has the formula $Li_xTiNb(PO_4)_3$, where $0 \leq x \leq 2$.

56. The battery of claim 28, wherein the cathode material has the formula $Li_{1+x}FeNb(PO_4)_3$, $0 \leq x \leq 2$.

25 57. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode comprising a rhombohedral NASICON material having the formula $Y_xM_2(PO_4)_y(XO_4)_{3-y}$, where $0 < y \leq 3$, M is a transition-metal atom, $0 \leq x \leq 5$, Y is Li or Na, and X = Si, As, or S.

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58. The battery of claim 34, wherein said cathode material has the formula $\text{Li}_{1+x}\text{Fe}_2(\text{PO}_4)(\text{SO}_4)_2$, where $0 \leq x \leq 2$.

59. A secondary battery comprising an anode, a cathode and an electrolyte, said cathode
5 comprising a rhombohedral NASICON material having the formula $\text{A}_{3-x}\text{V}_2(\text{PO}_4)_3$, where A may be Li, Na or a combination thereof and $0 \leq x \leq 2$.

~~60. The battery of claim 36, wherein the cathode material has the formula $\text{Li}_{2+x}\text{NaV}_2(\text{PO}_4)_3$, where $0 \leq x \leq 2$.~~

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61. A variable optical transmission device comprising transparent semi-conductor coated glass or plastic, and including at least one positive electrode and at least one negative electrode separated by a solid or gel electrolyte, wherein at least one electrode comprises a modified olivine compound as set forth in claim 23.

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